

POLYSILOXANE FOR USE IN ELECTROCHEMICAL CELLS

CROSS REFERENCE TO RELATED APPLICATION

5 [0001] This application is related to U.S. Patent Application serial number XXX, filed on XXX, entitled "Electrolyte Including Polysiloxane with Cyclic Carbonate Groups," which claims priority to U.S. Provisional Application serial number 60/502,017, filed September 10, 2003, entitled "Electrolyte Including Polysiloxane with Cyclic Carbonate Groups." Each of the above applications is incorporated herein in its entirety, including all disclosures submitted therewith.

10 [0002] This Application is also related to International Application PCT/US03/08783; filed on March 20, 2003; and entitled "Method for Fabricating Composite Electrodes" which claims priority to provisional application serial number 60/451,065; filed February 26, 2003; and entitled "Method for Fabricating Composite Electrodes"; and which also claims priority to provisional application serial number 60/443,892; filed January 30, 2003; and entitled

15 "Nonaqueous Liquid Electrolyte"; and which also claims priority to provisional application serial number 60/446,848; filed February 11, 2002; entitled "Polymer Electrolyte for Electrochemical Cell" and which also claims priority to PCT Application number PCT/US03/02127; filed January 22, 2003; and entitled "Nonaqueous Liquid Electrolyte" and which also claims priority to PCT/US03/02128; filed January 22, 2003; and entitled "Solid Polymer Electrolyte and Method

20 of Preparation" and which also claims priority to US Patent Application serial number 10/167,940; filed June 12, 2002; and entitled "Nonaqueous Liquid Electrolyte" which is a Continuation-in-Part of co-pending application Serial Number 10/104,352, filed March 22, 2002. Each of the above applications is incorporated herein in its entirety, including all disclosures submitted therewith.

25 [0003] This Application is also related to U.S. Patent Application 60/543,951, entitled "Siloxanes" and filed February 11, 2004 and U.S. Patent Application 60/543,898, entitled "Siloxane Based Electrolytes for Use in Electrochemical Devices" and filed February 11, 2004. Each of the above applications is incorporated herein in its entirety, including all disclosures submitted therewith.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0004] This invention was made with United States Government support under NIST ATP Award No. 70NANB043022 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in this invention pursuant to NIST ATP Award No. 70NANB043022 and pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago representing Argonne National Laboratory, and NIST 144 LM01, Subcontract No. AGT DTD 09/09/02.

FIELD

10 [0005] The present invention relates to electrolytes for electrochemical devices, and more particularly to electrolytes that include polysiloxanes.

BACKGROUND

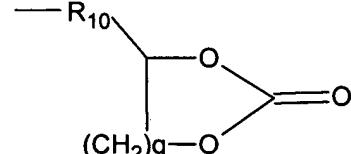
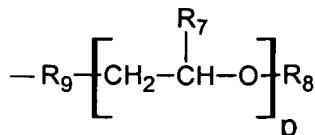
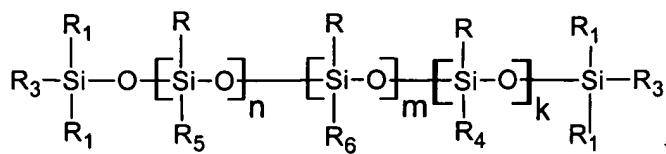
15 [0006] The increased demand for lithium batteries has resulted in research and development to improve the safety and performance of these batteries. Many batteries employ liquid electrolytes associated with high degrees of volatility, flammability, and chemical reactivity. A variety of polysiloxane polymer based electrolytes have been developed to address these issues. However, polysiloxane based electrolytes typically have a low ionic conductivity that limits their use to applications that do not require high rate performance. As a result, there is a need for polysiloxane-based electrolytes with an increased ionic conductivity.

20

SUMMARY

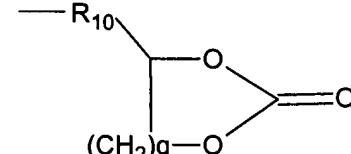
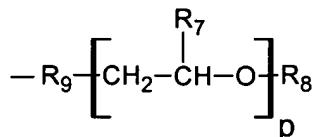
25 [0007] An electrolyte for use in an electrochemical device is disclosed. The device includes an electrolyte with a polysiloxane. The backbone of the polysiloxane includes one or more terminal silicons linked to a side chain that includes a poly(alkylene oxide) moiety or a cyclic carbonate moiety. The backbone can also include non-terminal silicons linked to side chains that include a poly(alkylene oxide) moiety or a carbonate moiety. In some instances, each silicon on the polysiloxane backbone is linked to at least one side chain that includes a poly(alkylene oxide) moiety or a carbonate moiety.

[0008] In some instances, the polysiloxane is represented by:



$R_3$  is represented by: ;  $R_4$  is a cross link

that links the polysiloxane backbone to another polysiloxane backbone;  $R_5$  is represented by:



5 ;  $R_6$  is represented by: ;  $R_7$  is hydrogen; alkyl or aryl;  $R_8$  is alkyl or aryl;  $R_9$  is oxygen or an organic spacer;  $R_{10}$  is an oxygen or an organic spacer;  $k$  is greater than or equal to 0;  $p$  is 3 to 20;  $q$  is 1 to 2;  $m$  is greater than or equal to 0 and  $n$  is 2 to 25.

[0009] A method of forming the electrolyte is also disclosed. The method includes 10 combining components of a precursor solution. The components include a polysiloxane precursor having a backbone with terminal silicones that are each linked to a hydrogen and a side-chain precursor that includes a poly(alkylene oxide) moiety or a carbonate moiety. The method can further include reacting the components of the precursor solution so as to form a polysiloxane having one or more terminal silicones that are each linked to at least one side chain 15 that includes a poly(alkylene oxide) moiety or a carbonate moiety. In some instances, a ring opening polymerization is employed to generate the polysiloxane precursor.

#### BRIEF DESCRIPTION OF THE FIGURES

[0010] Figure 1 illustrates an example of a method for employing hydrosilylation to 20 generate polysiloxanes having terminal silicones linked to side chains that include poly(alkylene oxide) moieties and/or carbonate moieties.

[0011] Figure 2 illustrates an example of a method for employing dehydrogenation to generate polysiloxanes having terminal silicons linked to side chains that include poly(alkylene oxide) moieties and/or carbonate moieties.

[0012] Figure 3 illustrates the method of Figure 2 adapted for generation of a polysiloxane having terminal side chains with a different structure than the non-terminal side chains.

[0013] Figure 4 illustrates an example of a method that employs ring-opening polymerization to form a polysiloxane precursor suitable for use in the method of Figure 1, Figure 2 or Figure 3.

[0014] Figure 5 illustrates a generalized reaction for generating a first side-chain precursor suitable for use in the reaction of Figure 1.

[0015] Figure 6 illustrates a generalized reaction for generating a first side-chain precursor suitable for use in the reaction of Figure 1.

15 DETAILED DESCRIPTION

[0016] An electrolyte suitable for use in electrochemical devices is disclosed. The electrolyte includes a polysiloxane. The polysiloxane backbone can include non-terminal silicons that are each linked to one or more non-terminal side chains. The non-terminal side chains can each include a poly(alkylene oxide) moiety. The polysiloxane backbone can also include one or more terminal silicons linked to terminal side chains that each include a poly(alkylene oxide) moiety. The use of terminal side chains with poly(alkylene oxide) moieties increases the number of poly(alkylene oxide) moieties associated with the polysiloxane. Because the poly(alkylene oxide) moieties serve as a source of ionic conductivity, increasing the number of poly(alkylene oxide) moieties associated with a polysiloxane increases the ionic conductivity of the polysiloxane and accordingly increases the ionic conductivity of the electrolyte. For instance, the electrolytes can provide an ionic conductivity better than  $1.0 \times 10^{-4}$  S/cm at 25 °C.

[0017] In some instances, each of the terminal silicons is linked to one or more terminal side chains that include a poly(alkylene oxide) moiety. A suitable poly(alkylene oxide) moiety

for the terminal side chains includes, but is not limited to, a poly(ethylene oxide) moiety. A spacer can be positioned between a terminal silicon and a poly(alkylene oxide) moiety. The spacer can be organic and in some instances, includes one or more CH<sub>2</sub> groups.

[0018] As noted above, the non-terminal silicons on the backbone can be linked to non-terminal side-chains that include a poly(alkylene oxide) moiety. A suitable poly(alkylene oxide) moiety for the non-terminal side chains includes, but is not limited to, a poly(ethylene oxide) moiety. A spacer can be positioned between a non-terminal silicon and a poly(alkylene oxide) moiety. The spacer can be organic and, in some instances, includes one or more CH<sub>2</sub> groups.

[0019] In some instances, a portion of the side chains include a carbonate moiety and a portion of the side chains include a poly(alkylene oxide) moiety. For instance, one or more of the terminal side chains and/or one or more of the non-terminal side chains can include a cyclic carbonate moiety. The cyclic carbonate moiety can have a high ability to dissociate the salts employed in battery electrolytes. As a result the cyclic carbonates can provide high concentrations of free ions in the electrolyte and the poly(alkylene oxide) moieties can act as substrates for ion coordination and transportation. As a result, the poly(alkylene oxide) moiety and the poly(alkylene oxide) moiety can act together to enhance the ionic conductivity of the electrolyte.

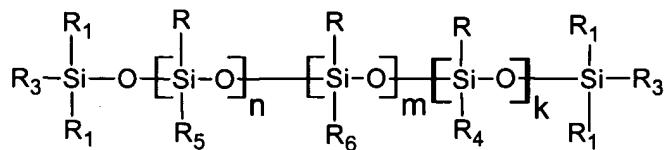
[0020] The terminal side chains can have different structures than the non-terminal side chains. For instance, the terminal side chains can include carbonate moieties while the non-terminal side chains include poly(alkylene) oxide moieties. Alternately, the non-terminal side chains and the terminal side chains can include poly(alkylene) oxide moieties but have different structures. For instance, the poly(alkylene) oxide moieties can be different or the structure linking the poly(alkylene) oxide moieties to the backbone can be different. In some instances, the terminal side chains have different structures.

[0021] These electrolytes can be liquids, solids or gels. For instance, the polysiloxanes are generally liquids at room temperature. As a result, the electrolyte can be a liquid. The polysiloxanes can also be cross-linked. In some instances, cross-linking of these polysiloxanes provides a solid or gel electrolyte. Accordingly, the electrolyte can also be a solid. Further, the above polysiloxanes can also be members of an interpenetrating network. As a result, the

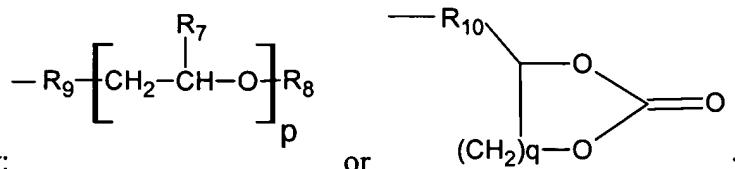
electrolyte can include an interpenetrating network. Additionally, an interpenetrating network can exist as a solid or gel. Accordingly, the interpenetrating network can serve as a mechanism for providing a solid electrolyte or a gel electrolyte.

**[0022]** Examples of suitable polysiloxanes have a structure according to General Formula

5 I:

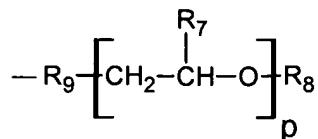


where R is alkyl or aryl; R<sub>1</sub> is alkyl or aryl;

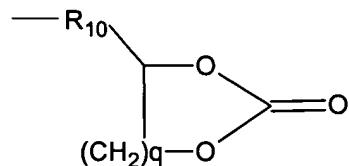


$R_3$  is represented by:

$R_4$  is a cross link that links the polysiloxane backbone to another polysiloxane backbone;



10  $R_5$  is represented by:



$R_6$  is represented by:  $(CH_2)_q-O'$

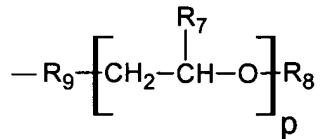
R<sub>7</sub> is hydrogen; alkyl or aryl; R<sub>8</sub> is alkyl or aryl; R<sub>9</sub> is oxygen or an organic spacer; R<sub>10</sub> is an oxygen or an organic spacer; k is greater than or equal to 0; p is 3 to 20; q is 1 to 2; m is greater

15 than or equal to 0 and n is greater than or equal to 1 and can be 2 to 25. In instances where m is greater than 0, a ratio of n:m can be 1:1 to 100:1 and is preferably 5:1 to 100:1. A suitable organic spacer can include one or more -CH<sub>2</sub>- groups. Other suitable spacers can include an alkylene, alkylene oxide, or bivalent ether moiety. These spacers can be substituted or unsubstituted. In one example, R<sub>9</sub> is represented by: -O-(CH<sub>2</sub>)<sub>3</sub>-O- or -(CH<sub>2</sub>)<sub>3</sub>-O- with the

oxygen linked to the polyethylene oxide moiety. In another example, R<sub>10</sub> is represented by: -CH<sub>2</sub>-O-(CH<sub>2</sub>)<sub>3</sub>- where the single -CH<sub>2</sub>- group is positioned between the carbonate and the oxygen or -CH<sub>2</sub>-O-.

5 [0023] In instances, where a polysiloxane according to Formula I includes one or more cross links, a suitable ratio for (number of cross links) :(m+n) includes, but is not limited to, a ratio in a range of 1:4 to 1:200, in a range of 1:6 to 1:100, or in a range of 1:6 to 1:70.

10 [0024] Each of the R<sub>3</sub> can be the same or different. In some instances, one of the R<sub>3</sub> includes a poly(alkylene oxide) moiety and another R<sub>3</sub> includes a cyclic carbonate moiety. The structures of R<sub>3</sub> can be the same as the structure of R<sub>5</sub>. In some instances, the R<sub>3</sub> structures are different from the R<sub>5</sub> structures. When m is greater than 0, the structures of R<sub>3</sub> can be the same as the structure of R<sub>6</sub>. In some instances, the R<sub>3</sub> structures are different from the structure of R<sub>6</sub>. In some instances, m is 0 and R<sub>3</sub> and R<sub>5</sub> each have a structure according



to: and the structures for R<sub>3</sub> are different from the structure for R<sub>5</sub> or the same as the structure for R<sub>5</sub>.

15 [0025] When a polysiloxane according to General Formula I is to be employed in an electrolyte, a suitable average molecular weight for the polysiloxane includes, but is not limited to, an average molecular weight less than or equal to 3000 g/mole.

20 [0026] An electrolyte for use in an electrochemical device can be generated by dissolving one or more salts in the polysiloxane. In instances where the electrolyte is to be solidified or gelled, the salt is preferably dissolved in the electrolyte before solidification or gelling of the electrolyte. These polysiloxanes can dissolve a variety of salts including, but not limited to, salts that include lithium and salts that exclude lithium. As a result, the polysiloxane is suitable for use in the electrolytes of electrochemical devices such as primary batteries, secondary batteries, and capacitors. Suitable lithium salts for dissolving in the polysiloxane include, but 25 are not limited to, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C, LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>, lithium alkyl fluorophosphates, lithium bis(oxalato)borate (LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>), as well as other lithium bis(chelato)borates having five to seven membered rings, LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, LiPF<sub>3</sub>(CF<sub>3</sub>)<sub>3</sub>, and mixtures thereof.

[0027] The concentration of the salt in the electrolyte can be characterized by an [EO]/[Li] ratio, where [EO] is the molar concentration of the active oxygens in the electrolyte and [Li] is the molar concentration of the lithium salt in the electrolyte. Because [EO] is directed to active oxygens, a polysiloxane having a structure according to Formula I includes p active oxygens in the poly(ethylene oxide) moieties and 3 active oxygens in the cyclic carbonate moieties. In some instances, a spacer includes active oxygens. For instance, an R<sub>5</sub> side chain includes p+1 active oxygens when R<sub>9</sub> is -O-(CH<sub>2</sub>)<sub>3</sub>- with the oxygen linked to the poly(ethylene oxide) moiety. The electrolyte can be generated so as to have an [EO]/[Li] ratio of 5 to 50. If the [EO]/[Li] ratio is larger than 50, the ionic conductivity of the resulting polymeric electrolyte can decrease undesirably because of the inadequate numbers of carrier ions in the electrolyte. If the [EO]/[Li] ratio is smaller than 5, the salt may not sufficiently dissociate and the aggregated lithium ions can reduce the ionic conductivity.

[0028] In some instances, the electrolyte is generated so as to include one or more additives. Additives can serve a variety of different functions. For instance, additives can enhance the ionic conductivity and/or enhance the voltage stability of the electrolyte. A preferred additive forms a passivation layer on one or more electrodes in an electrochemical device such as a battery or a capacitor. The passivation layer can enhance the cycling capabilities of the electrochemical device. In one example, the passivation layer is formed by reduction of the additive at the surface of an electrode that includes carbon. In another example, the additive forms a polymer on the surface of an electrode that includes carbon. The polymer layer can serve as the passivation layer.

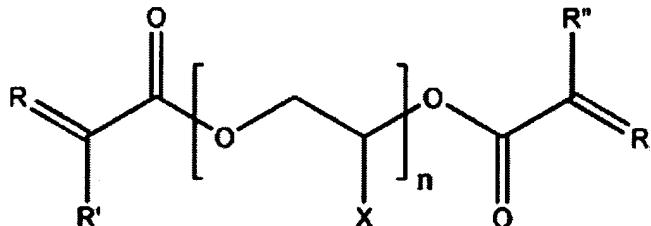
[0029] Suitable additives include, but are not limited to, carbonates, sulfur compounds, unsaturated hydrocarbons and nitrogen compounds. In some instances, the electrolyte includes at least one additive selected from the group consisting of: vinyl carbonate (VC), vinyl ethylene carbonate (VEC), ethylene sulfite, 1,3 dimethyl butadiene, styrene carbonate, aromatic carbonates, vinyl pyrrole, vinyl piperazine, vinyl piperidine, vinyl pyridine, and mixtures thereof. In one example, the electrolyte includes vinyl ethylene carbonate as an additive. VC is an example of an additive that can be reduced to form a passivation layer that includes a carbonate at the surface of an electrode that includes carbon. Pyridine is an example of an additive that can form a polymeric passivation layer at the surface of an electrode that includes carbon. VEC is an example of an additive that can form a passivation layer by both being reduced and forming

a polymer at the surface of an electrode that includes carbon. A suitable concentration for an additive in the electrolyte includes, but is not limited to, concentrations greater than 0.1 wt%, greater than 0.5 wt% and/or less than 5 wt% or less than 20 wt%.

5 [0030] The electrolyte can include a network polymer that forms an interpenetrating network with the polysiloxane. An electrolyte having an interpenetrating network can be generated by polymerizing and/or cross-linking one or more network polymers in the presence of the polysiloxane or by polymerizing and/or cross-linking the polysiloxane in the presence of one or more network polymers. Alternately, an electrolyte having an interpenetrating network can be generated by polymerizing and/or cross-linking one or more network polymers and the 10 polysiloxane in the presence of one another.

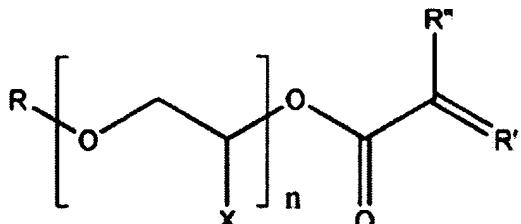
15 [0031] Suitable network monomers from which the network polymer can be formed include, but are not limited to, acrylates and methacrylates. Acrylates and/or methacrylates having one or more functionalities can form a polyacrylate and/or a polymethacrylate network polymer. Acrylates and/or methacrylates having two or more functionalities can both 20 polymerize and cross-link to form a cross-linked polyacrylate network polymer and/or to form a cross-linked polymethacrylate network polymer. In some instances, acrylates and/or methacrylates having four or more functionalities are a preferred network monomer. Suitable acrylates include, but are not limited to, poly(alkylene glycol) dialkyl acrylate. Suitable methacrylates include, but are not limited to, poly(alkylene glycol) dialkyl methacrylate.

20 [0032] A suitable network monomer is represented by the following Formula III:



25 wherein: R is an alkylidene, a carbene, or is represented by CR'''R'''' and each R can be the same or different; R' represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R'' represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R''' represents hydrogen or an alkyl group having 1 to 10 carbon atoms; R'''' represents hydrogen or an alkyl group having 1 to 10 carbon atoms; X is hydrogen or a methyl group; and n represents a numeral of 1 to 15.

[0033] When a monomer that cross-links is employed to form a cross-linked network polymer, a control monomer can be employed to control cross-linking density. A suitable control monomer for use with a network monomer according to Formula III is represented by the



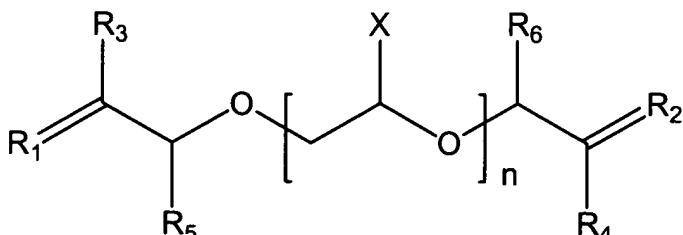
following Formula IV:

wherein: R is an alkyl group

5 having 1 to 10 carbon atoms; R' is an alkylidene, a carbene, or is represented by CR'''R'''' is represented by =CR'''R''''; R'' is hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R''' represents hydrogen or an alkyl group having 1 to 10 carbon atoms; R'''' represents hydrogen or an alkyl group having 1 to 10 carbon atoms; X is hydrogen or a methyl group; and n represents a whole number from 1 to 20. During formation  
10 of the network polymer, the illustrated control monomer serves as a co-monomer with the network monomers according to Formula III. Because the control monomer does not cross link, increasing the amount of control monomer present during formation of the network polymer can reduce the density of cross linking.

[0034] Diallyl terminated compounds can also be employed as a network monomer.

15 Diallyl terminated compounds having two or more functionalities can polymerize and cross-link to form the network polymer. An example of a diallyl terminated compound having two functionalities that allow the compound to polymerize and cross link is represented by Formula V.



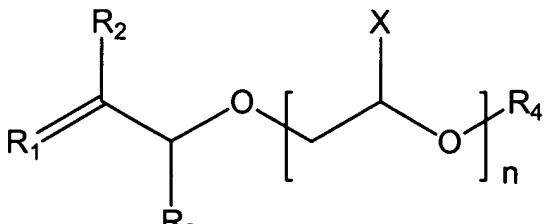
Formula V: : wherein R<sub>1</sub> represents an

20 alkylidene, a carbene, or CR'''R''''; R<sub>2</sub> represents an alkylidene, a carbene, or CR'''R''''; R<sub>3</sub> represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sub>4</sub> represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sub>5</sub> represents hydrogen or an alkyl group having 1 to

10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sub>6</sub> represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sup>'''</sup> represents hydrogen or an alkyl group having 1 to 10 carbon atoms; R<sup>''''</sup> represents hydrogen or an alkyl group having 1 to 10 carbon atoms; X is hydrogen or a methyl group; and n represents a

5 numeral of 1 to 15.

[0035] Formula VI represents an example of a control monomer for controlling the cross linking density of a compound represented by Formula V.



Formula VI: : wherein R<sub>1</sub> represents an alkylidene, a carbene, or is represented by CR<sup>'''</sup>R<sup>''''</sup>; R<sub>2</sub> represents hydrogen or an alkyl group having 1 to

10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sub>3</sub> represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sub>4</sub> represents hydrogen or an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; R<sup>'''</sup> represents hydrogen or an alkyl group having 1 to 10 carbon atoms; R<sup>''''</sup> represents hydrogen or an alkyl group having 1 to 10 carbon atoms; X is hydrogen or a methyl group; and n represents a numeral of 1 to 15.

[0036] A diallyl terminated compound suitable for serving as a network monomer can include more than two functionalities. For instance, the oxygens shown in Formula III can be replaced with CH<sub>2</sub> groups to provide a diallyl terminated compound having four functionalities that allow the compound to polymerize and cross link. Further, the oxygens shown in Formula

20 IV can be replaced with CH<sub>2</sub> groups to provide an example of a control monomer for controlling the cross linking density of the diallyl terminated compound. Other suitable diallyl terminated compounds for serving as a network monomer include, but are not limited to, poly(alkylene glycol) diallyl ether. A specific example includes, but is not limited to, tetra(ethylene glycol) diallyl ether.

25 [0037] An electrolyte that includes an interpenetrating network can be formed by generating a precursor solution that includes the one or more polysiloxanes, the monomers for

forming the cross-linked network polymer and one or more salts. Suitable salts include, but are not limited to, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C, LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>, lithium bis(chelato)borate including lithium(oxalato)borate (LiBOB), and lithium alkyl fluorophosphates. The precursor solution can also optionally be generated so as to 5 include one or more radical initiators and/or one or more additives. Suitable radical initiators include, but are not limited to, thermal initiators including azo compounds such as azoisobutyronitrile, peroxide compounds such as benzoylperoxide, and bismaleimide. A control monomer can also optionally be added to the precursor solution to control the cross-linking density of the network monomer. The monomers are cross-linked and/or polymerized 10 to form the electrolyte. In some instance, the temperature of the precursor solution is elevated and/or the precursor solution is exposed to UV to form the electrolyte. The resulting electrolyte can be a liquid, solid or gel. The physical state of the electrolyte can depend on the ratio of the components in the precursor solution.

[0038] An electrolyte having an interpenetrating network can also be generated from a 15 polymer and a cross-linking agent for cross linking of the polymer. For instance, a diallyl terminated compound can serve as a cross linking agent for a polysiloxane having a backbone that includes one or more silicons linked to a hydrogen. Examples of suitable diallyl terminated cross-linking agents include, but are not limited to, diallyl-terminated polysiloxanes, diallyl 20 terminated polysiloxanes, diallyl terminated alkylene glycols and diallyl terminated poly(alkylene glycol)s.

[0039] The electrolyte can be generated by preparing a precursor solution that includes the polymer, the cross linking agent, the one or more polysiloxanes and one or more salts. The precursor solution can also optionally be generated so as to include one or more catalysts, and/or one or more additives. Suitable catalysts include, but are not limited to, platinum catalysts such 25 as Karstedt's catalyst and H<sub>2</sub>PtCl<sub>6</sub>. In some instances, an inhibitor is added to the precursor solution to slow the cross-linking reaction enough to permit handling prior to viscosity changing. Suitable inhibitors include, but are not limited to, dibutyl maleate. The polymer is cross-linked to form the electrolyte. In some instances, heat and/or UV energy is also applied to the precursor solution during the reaction of the cross linking precursor and the cross-linking agent.

[0040] A network polymer suitable for the interpenetrating network can be formed using other precursors. For instance, the network polymer can be generated from a mixture of monomers and cross-linking agents that are different from one another. The monomers can polymerize and the cross-linking agents can provide cross linking of the resulting polymer.

5 Other examples of methods for generating electrolytes and electrochemical devices that include network polymers are described in U.S. Patent application serial number 10/104,352, filed on March 22, 2002, entitled "Solid Polymer Electrolyte and Method of Preparation" and incorporated herein by reference in its entirety.

[0041] As noted above, the electrolyte can include one or more solid polymers in 10 addition to one or more polysiloxanes. The solid polymers are each a solid when standing alone at room temperature. As a result, the ratio of solid polymer to the other electrolyte components can be selected so as to provide an electrolyte that is a solid at room temperature. A suitable solid polymer is an aprotic polar polymer or aprotic rubbery polymer. Examples of 15 suitable solid polymers include, but are not limited to, polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene), polystyrene, polyvinyl chloride, poly(alkyl methacrylate), poly(alkyl acrylate), styrene butadiene rubber (SBR), poly(vinyl acetate), poly(ethylene oxide) (PEO) and mixtures thereof.

[0042] The electrolyte can be generated by preparing a precursor solution that includes 20 one or more of the polysiloxanes and a solution that includes a solid polymer. The solution can be generated by dissolving the solid polymer in a solvent such as N-methylpyrrolidone (NMP), dimethyl formamide, dimethyl acetamide, tetrahydrofuran, acetonitrile, and/or water. One or more additives can be optionally added to the precursor solution. One or more salts can be added to the precursor solution or the salt can be dissolved in a component of the precursor 25 solution before adding the component to the precursor solution. A solid electrolyte can be formed by evaporating the solvent from the precursor solution.

[0043] An electrolyte that includes one or more solid polymers can also be generated by 30 polymerizing a solid polymer in the presence of the polysiloxane. For instance, a precursor solution can be generated so as to include one or more polysiloxanes, monomers for the solid polymer and a radical initiator. Suitable radical initiators include, but are not limited to,

thermal initiators including azo compounds such as azoisobutyronitrile, peroxide compounds such as benzoylperoxide, and bismaleimide. The precursor solution can optionally be prepared so as to include one or more additives. One or more salts can be added to the precursor solution or the salt can be dissolved in a component of the precursor solution before adding the 5 component to the precursor solution. The electrolyte can be formed by polymerizing the monomers. As an example, an acrylonitrile monomers can be mixed with the polysiloxane. The acrylonitrile monomers can be polymerized by the application of heat and/or UV to form an electrolyte having a polyacrylonitrile solid polymer.

10 [0044] As is evident from the above discussion, the electrolyte can include components in addition to the one or more polysiloxanes. For instance, the electrolyte can include salts, additives, network polymers and/or solids polymers. In some instances, the electrolyte is generated such that the one or more polysiloxanes are more than 20 wt% of the electrolyte, more than 50 wt% of the electrolyte, more than 80 wt% of the electrolyte or more than 95 wt% of the electrolyte.

15 [0045] Suitable polysiloxanes can be generated using a hydrosilylation reaction with reactants that include a polysiloxane precursor and side-chain precursors. A suitable polysiloxane precursor includes terminal silicons and non-terminal silicons that are linked to a hydrogen. Suitable side-chain precursors include a poly(alkylene oxide) moiety linked to an allyl terminated spacer precursor or a carbonate moiety linked to an allyl terminated spacer 20 precursor.

25 [0046] Figure 1 illustrates an example of a method for employing hydrosilylation to generate the above polysiloxanes. The method includes forming a precursor solution by mixing a precursor polysiloxane labeled A, a first side-chain precursor component labeled B and a second side-chain precursor component labeled C. The precursor polysiloxane includes a backbone with  $n+m$  non-terminal silicons and two terminal silicons. Each of the terminal silicons and the non-terminal silicons are linked to a hydrogen. The first side-chain precursor includes an allyl-terminated spacer precursor represented by  $-R_{11}-CH=CH_2$  where  $R_{11}$  can be nil or organic. For instance,  $R_{11}$  can include one or more  $CH_2$  groups. Further,  $R_{11}$  can include an alkylene, alkylene oxide or a bivalent ether moiety and can be substituted or unsubstituted. In 30 one example,  $R_{11}$  represents  $-O-CH_2-$  with the oxygen linked to the poly(ethylene oxide) moiety.

The second side-chain precursor includes an allyl-terminated spacer precursor represented by – R<sub>12</sub>-CH=CH<sub>2</sub> where R<sub>12</sub> can be nil or organic. For instance, R<sub>12</sub> can include one or more CH<sub>2</sub> groups. Further, R<sub>12</sub> can include an alkylene, alkylene oxide or a bivalent ether moiety and can be substituted or unsubstituted. In one example, R<sub>12</sub> represents -CH<sub>2</sub>-O-CH<sub>2</sub>-.

5 The remaining variables shown in Figure 1 are defined with respect to Formula I.

[0047] In some instances, a reaction solvent is added to the precursor solution of Figure 1. A suitable solvent includes, but is not limited to, toluene, THF, and benzene. A catalyst can be added to the precursor solution to catalyze the hydrosilylation reaction. Suitable catalysts for use in the precursor solution include, but are not limited to, platinum catalysts such 10 as Karstedt's catalyst (divinyltetramethyldisiloxane (Pt(dvs)), dicyclopentadiene platinum(II) dichloride, H<sub>2</sub>PtCl<sub>6</sub>. In some instances, heat is applied to the precursor solution to react the components of the precursor solution. The reaction can be continued until the Si-H groups are no longer evident on an FTIR spectrum. The product solution can be distilled to remove any unreacted side-chain precursors and/or reaction solvent. In some instances, the product is 15 purified by distillation. The product can be purified by distillation using a long vacuum-jacketed Vigreux column and/or by sequentially performing two or more regular distillations. The regular distillations can be vacuum distillations. When a sequence of two or more regular distillations is performed, a central fraction of the distillate can be used as the product for each distillation step.

[0048] Suitable polysiloxanes can also be generated using a dehydrogenation reaction 20 between a polysiloxane precursor and side-chain precursors. A suitable polysiloxane precursor includes terminal silicons and non-terminal silicons. The non-terminal silicons and the terminal silicons are each linked to a hydrogen. A suitable first side chain precursor includes a poly(alkylene oxide) moiety and a terminal -OH group or a cyclic carbonate moiety and a 25 terminal -OH group.

[0049] Figure 2 illustrates an example of a method for employing dehydrogenation to 30 generate the above polysiloxanes. The method includes forming a precursor solution by mixing a precursor polysiloxane labeled A, a first side-chain precursor labeled B and a second side chain precursor labeled C. The precursor polysiloxane includes a backbone with n+m non-terminal silicons and two terminal silicons. The terminal silicons and the non-terminal silicons are each

linked to a hydrogen. The first side chain precursor includes an -OH terminated spacer precursor represented by -R<sub>14</sub>-OH where R<sub>14</sub> can be nil or organic. For instance, R<sub>14</sub> can include one or more CH<sub>2</sub> groups. Further, R<sub>14</sub> can be an alkylene, alkylene oxide or a bivalent ether moiety and can be substituted or unsubstituted. The second side-chain precursor includes 5 an -OH terminated spacer precursor represented by -R<sub>15</sub>-OH where R<sub>15</sub> can be nil or organic. For instance, R<sub>15</sub> can include one or more CH<sub>2</sub> groups. Further, R<sub>15</sub> can be an alkylene, alkylene oxide or a bivalent ether moiety and can be substituted or unsubstituted. The remaining variables shown in Figure 1 are defined with respect to Formula I.

[0050] In some instances, a reaction solvent is added to the precursor solution of Figure 10 2. A suitable solvent includes, but is not limited to, Toluene. In some instances, a catalyst is added to the precursor solution to catalyze the dehydrogenation reaction. Suitable catalysts for use in the precursor solution include, but are not limited to, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Rhodium catalyst (Rh(Ph<sub>3</sub>P)<sub>3</sub>Cl) and/or Palladium catalyst (Pd<sub>2</sub>(dba)<sub>3</sub>). In some instances, heat 15 is applied to the precursor solution to react the components of the precursor solution. The reaction can be continued until the Si-H groups are no longer evident on an NMR spectrum. The product solution can be distilled to remove any unreacted side-chain precursors and/or reaction solvent. In some instances, the product is purified by distillation. The product can be purified by distillation using a long vacuum-jacketed Vigreux column and/or by sequentially performing two or more regular distillations. The regular distillations can be vacuum 20 distillations. When a sequence of two or more regular distillations is performed, a central fraction of the distillate can be used as the product for each distillation step.

[0051] Although Figure 1 and Figure 2 each illustrate the terminal silicons in the product 25 polysiloxane linked with a side chain that includes a poly(alkylene oxide), these methods can provide a random distribution of the side chains among the silicons. For instance, one or both of the terminal silicons can react with a second side chain precursor. As a result, these methods can provide product polysiloxanes that include a terminal silicon linked to a side chain that includes a poly(alkylene oxide) moiety and another terminal silicon linked to a side chain that includes a carbonate moiety. Further, these methods can provide product polysiloxanes that 30 include terminal silicons that are each linked to a side chain that includes a cyclic carbonate moiety.

[0052] A precursor ratio can be employed to characterize the concentrations of the components in the precursor solutions of Figure 1 or Figure 2. The precursor ratio is the ratio of (the molar concentration of the side-chain precursor in the precursor solution) to (the molar concentration of the Si-H groups on the backbone of the polysiloxane precursor). When the 5 precursor ratio is greater than 1, the hydrogens in each Si-H group can be replaced with a side chain. As a result, the Si-H groups on backbone of the polysiloxane precursor can be depleted during the reaction of the precursor solution. In some instances, the precursor ratio is greater than 1 to ensure that each of the Si-H groups is replaced by a silicon to side-chain link. Other suitable precursor ratios include, but are not limited to, precursor ratios greater than 1.1 and/or 10 less than 3:1. In some instances, a precursor ratio is employed that is sufficiently low to generate a product polysiloxane having one or more Si-H groups. As will become evident below, product polysiloxanes with one or more Si-H groups can be employed to generate a cross linked polysiloxane.

[0053] A side-chain precursor ratio can also be employed to characterize the ratio of the 15 components in the precursor solution. The side-chain precursor ratio is the ratio of the molar concentration of the first side-chain precursor in the precursor solution to the molar concentration of the second side-chain precursor in the precursor solution. The side-chain precursor ratio affects the ratio of n:m in the product polysiloxane. For instance, increasing the side-chain precursor ratio increases the ratio of n:m. Suitable side-chain precursor ratios 20 include, but are not limited to, ratios less than 20:1. In some instances, second side chain precursor is not added to the precursor solution to provide a product polysiloxane with m = 0. In these instances, when the reaction is taken to saturation, the terminal and non-terminal silicons are each linked to a side chain that includes a poly(alkylene oxide) moiety.

[0054] The method illustrated in Figure 1 and Figure 2 can be adapted for generation of a 25 polysiloxane having terminal side chains with a different structure than the non-terminal side chains. For instance, the polysiloxane precursor can include non-terminal silicons linked to side chains and terminal silicons linked to hydrogens. As a result, the side chain precursors of Figure 1 and Figure 2 react with the terminal silicons. Because the terminal side-chains and the non-terminal side chains are added to the backbone in different steps the terminal side-chains and 30 the non-terminal side chains can have different structures. For instance, the terminal side chains can include a cyclic carbonate moiety and the non-terminal side chains can include a

poly(alkylene oxide) moiety. As another example, the terminal side chains and the non-terminal side chains can have different structures but each include a poly(alkylene oxide) moieties.

[0055] Figure 3 illustrates the method of Figure 2 adapted for generation of a polysiloxane having terminal side chains with a different structure than the non-terminal side chains. The non-terminal silicons on the polysiloxane precursor include side chains,  $R_5$  and  $R_6$ , substituted for the non-terminal hydrogens evident in Figure 2. The terminal silicons are each linked to a hydrogen. The side chain precursors react with the terminal silicons. Although Figure 3 illustrates a first side chain precursor reacting with one terminal silicon and a second side chain precursor reacting with another terminal silicon, each of the terminal silicons can react with a first side chain precursor or each of the terminal silicons can react with a second side chain precursor. In some instances, second side chain precursors are not added to the precursor solution to provide a product polysiloxane having terminal silicons that are each linked to a side chain that includes a poly(alkylene oxide) moiety. In some instances, first side chain precursors are not added to the precursor solution to provide a product polysiloxane having terminal silicons that are each linked to a side chain that includes a cyclic carbonate moiety. Further, a polysiloxane precursor can be used with  $m = 0$  to provide a polysiloxane having each terminal silicon linked to at least one side chain that includes a carbonate moiety and non-terminal silicon that are each linked to at least one side chain that includes a poly(alkylene oxide) moiety.

[0056] The method of Figure 1 can also be adapted for generation of polysiloxanes having terminal side chains with a different structure than the non-terminal side chains. For instance, the method illustrated in Figure 1 can be employed using the polysiloxane precursor of Figure 3 in conjunction with the side chain precursors illustrated in Figure 1.

[0057] A ring opening polymerization can be employed to generate a polysiloxane precursor suitable for use in the methods of Figure 1, Figure 2 or Figure 3. Figure 4 illustrates an example of a method that employs ring-opening polymerization to form a polysiloxane precursor (labeled C). The method includes forming a precursor solution that includes a cyclic polysiloxane monomer labeled A where:  $i$  is greater than 0,  $j$  is greater than or equal to 0,  $(i+j)$  is 3 to 10;  $R_{16}$  can be a hydrogen or  $R_5$  and  $R_{17}$  can be a hydrogen or  $R_6$ . The precursor solution also includes a molecular weight controller labeled B. The molecular weight controller serves

as a source of ions for terminating the polymerization reaction. The illustrated molecular weight controller includes two silicons that are each linked to a hydrogen. These silicons become the terminal silicons on the polysiloxane precursor. When a polysiloxane precursor according to Figure 1 and Figure 2 is desired,  $R_{16}$  can be hydrogen and  $j$  can be 0. When a polysiloxane precursor according to Figure 3 is desired,  $R_{16}$  can be  $R_5$  and  $R_{17}$  can be  $R_6$  and the values of  $i$  and  $j$  are chosen to provide the desired ratio of  $m$  and  $n$ .

[0058] The concentration of the molecular weight controller in the solution can be adjusted to control the molecular weight of the polysiloxane precursor. For instance, adjusting the molar ratio of the controller to the cyclic polysiloxane in the precursor solution can change the value of  $n$  in the precursor polysiloxane. Increasing the molar concentration of the controller relative to the molar concentration of the cyclic polysiloxane can reduce the value of  $n+m$  while decreasing the molar concentration of the controller relative to the molar concentration of the cyclic polysiloxane can increase the value of  $n+m$ . A suitable ratio for the molar ratio of the controller to the cyclic polysiloxane includes, but is not limited to, ratios greater than 1:0.9 and/or less than 1:7. Although Figure 4 illustrates a single cyclic polysiloxane in the precursor solution, different cyclic polysiloxanes can be employed in the precursor solution. For instance, the illustrated product polysiloxane can be generated by preparing a precursor solution that includes a first cyclic polysiloxane with  $i = 0$  and a second cyclic polysiloxane with  $j = 0$ .

[0059] In some instances, a cation initiator is added to the precursor solution of Figure 3. A suitable cation initiator includes, but is not limited to, strong acids such as sulfuric acid,  $CF_3SO_3H$ , and  $HCl$ . In some instances, a reaction solvent can be added to the precursor solution of Figure 4. Heat can optionally be applied to the precursor solution to react the components of the precursor solution.

[0060] As noted above, the terminal silicons in the polysiloxane backbone may be linked to more than one side chain that includes a poly(alkylene oxide) moiety or a carbonate moiety. This result can be effectuated when one or more of the  $R_i$  in the molecular weight controller of Figure 4 is a hydrogen and the resulting polysiloxane precursor is employed in the method of Figure 1, Figure 2 or Figure 3. Additionally, the non-terminal silicons in the polysiloxane backbone may be linked to more than one side chain. This result can be effectuated when one

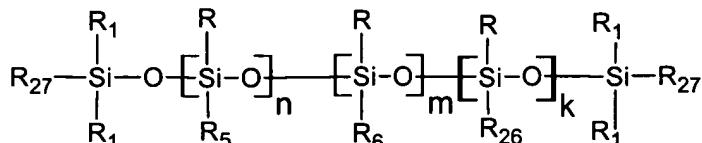
or more of the R in the cyclic polysiloxane of Figure 4 is a hydrogen and the resulting polysiloxane precursor is employed in the method of Figure 1, Figure 2 or Figure 3. Further, polysiloxanes having only one terminal silicon linked to a side chain that includes a poly(alkylene oxide) moiety can be effectuated when a hydrogen in the molecular weight controller of Figure 4 is replaced with an alkyl group and the resulting polysiloxane precursor is employed in the method of Figure 1, Figure 2 or Figure 3.

[0061] Suitable methods for generating cyclic polysiloxane monomers suitable for use in the method of Figure 4 is disclosed in PCT application number PCT US0308779, filed March 20, 2003 entitled “Polymer electrolyte for electrochemical cell” and incorporated herein in its entirety. Suitable method for generating a cyclic polysiloxane monomers suitable for use in the method of Figure 4 are also disclosed in U.S. Patent Application serial number 10/663024, filed on 9/15/03, and entitled “Electrolyte for Electrochemical Cell” and incorporated herein in its entirety which is a continuation in part of U.S. Patent Application serial number 10/663023, filed on 9/15/03, entitled “Polymer Electrolyte System” and incorporated herein its entirety.

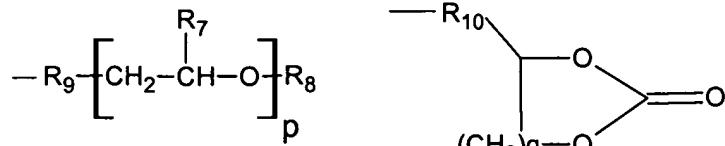
[0062] Figure 5 illustrates a method for generating a side-chain precursor suitable for use in the reaction of Figure 1. The illustrated reaction is suitable for generating a side chain with a spacer that includes an oxygen. Accordingly, the moiety represented by  $-R_{11}-$  in Figure 1 is represented by  $-R_{18}-O-$  in Figure 5. The other variables shown in Figure 5 are defined above. The reaction can occur in the presence of heat and/or a catalyst. Suitable catalysts include, but are not limited to, potassium tert-butoxide (t-BuOK), NaOH, and/or NaH. Figure 6 illustrates a method for generating a side chain precursor suitable for use in the reaction of Figure 1. The variables shown in Figure 3 are defined above. The reaction can occur in the presence of heat and/or a catalyst. Suitable catalysts include, but are not limited to,  $K_2CO_3$  and/or carbonate salts of the group IA metals such as  $Na_2CO_3$ . Additional techniques for generation of the above polysiloxanes and precursors are presented in U.S. Provisional Application serial number 60/502,017, filed September 10, 2003, entitled “Electrolyte Including Polysiloxane with Cyclic Carbonate Groups” and incorporated herein in its entirety.

[0063] As noted above, the polysiloxane can be cross linked. For instance, one or more of the silicones in the backbone can be linked to a cross linker that links the backbone to another

polysiloxane backbone. The polysiloxanes can be cross linked by generating a cross linking precursor having polysiloxane backbone with a portion of the silicons linked to a hydrogen. An example of a suitable cross linking precursor is a polysiloxane represented by the following



Formula II: ; where  $R_{27}$  is hydrogen or is



5 represented by and each  $R_{27}$  can be the same or different;  $R_{26}$  is hydrogen;  $k$  is greater than 0 or at least one  $R_{27}$  is a hydrogen and the remaining variables are defined with respect to Formula I. Suitable cross linking precursors can be generated by performing one of the methods in Figure 1 through Figure 3 with an excess of polysiloxane precursor. The excess polysiloxane precursor causes a portion of the Si-H links 10 that are present in the polysiloxane precursor to be present in the product polysiloxane.

[0064] A cross linking precursor can be reacted with a cross-linking agent to generate a cross-linked polysiloxane. Suitable cross-linking agents include, but are not limited to, compounds terminated with two or more allyl groups. Examples of suitable cross-linking agents include diallyl-terminated polysiloxane, diallyl terminated polysiloxanes, diallyl 15 terminated alkylene glycols and diallyl terminated poly(alkylene glycol)s. Suitable cross-linking agents can be represented by:  $CH_2=CH-CH_2-R_{20}-CH_2-CH=CH_2$ , where  $R_{20}$  is a moiety selected from the group consisting of  $O-(CH_2CH_2O)_s$  and  $Si-O-(Si-O)_t-Si$ , where  $s$  is at least 4 and less than 30, and  $t$  is at least 5 and less than 30. A suitable method for generating these 20 cross-linking agents includes, but is not limited to, the methods disclosed in U.S. patent application serial number 10/367,013, filed February 13, 2003, entitled "Cross-Linked Polysiloxanes" and incorporated herein in its entirety. When these cross-linking agents are employed to cross-link a cross link precursor having a portion of the backbone silicons linked to a hydrogen, at least a portion of the Si-H links in the backbone of the cross link precursor are replaced with an Si-C link between the silicon and the terminal carbon on the cross linking agent. 25 Accordingly, the cross-link represented by  $R_4$  in Formula I can be represented by:  $-CH_2-CH_2-CH_2-R_{20}-CH_2-CH_2-CH_2-$ , where  $R_{20}$  is a moiety selected from the group consisting of  $O-$

(CH<sub>2</sub>CH<sub>2</sub>O)<sub>s</sub> and Si-O-(Si-O)<sub>t</sub>-Si, where s is at least 4 and less than 30, and t is at least 5 and less than 30.

[0065] The cross links can be randomly distributed among the silicons on the backbone. For instance, employing the method of Figure 1 or Figure 2 to generate the cross linking precursor can provide a cross linking precursor with an essentially random distribution of Si-H groups along the backbone. Because the Si-H groups have a random distribution, the resulting cross links also have a random distribution.

[0066] A silicon in the backbone can be linked to more than one cross link. For instance, one or more of the R and/or one or more R<sub>16</sub> in the cyclic polysiloxane of Figure 4 can be a hydrogen. An excess of the resulting polysiloxane precursor can be employed in the method of Figure 1, Figure 2 or Figure 3. In some instances, a portion of the silicons in the product polysiloxane will be linked to more than one hydrogen. When this product polysiloxane is employed as the cross link precursor, one or more silicons can be linked to more than one cross link.

[0067] An electrolyte that includes the cross linked polysiloxane can be generated by mixing the cross linking precursor and the cross linking agent in a precursor solution. In some instances, a catalyst is added to the precursor solution to catalyze the interaction between the polysiloxane polymer and the cross-linking agent. Suitable catalysts include, but are not limited to, platinum catalysts such as Karstedt's catalyst and H<sub>2</sub>PtCl<sub>6</sub>. In some instances, an inhibitor is added to the precursor solution to slow the cross-linking reaction enough to permit handling prior to viscosity changing. Suitable inhibitors include, but are not limited to, dibutyl maleate. In some instances, heat is also applied to the precursor solution during the reaction of the cross linking precursor and the cross-linking agent.

[0068] In some instances, heating can solidify an electrolyte that includes a cross-linked polysiloxane. The cross-linking mechanism and/or the cross-linking density can determine the degree of solidification upon heating. In instances where the electrolyte solidifies, one or more salts can be added to the precursor solution prior to the solidification of the electrolyte. When the electrolyte that includes a cross-linked polysiloxane does not solidify, the electrolyte can be used in a liquid or gel form.

[0069] EXAMPLE 1 (p~3)

[0070] The generalized reaction illustrated in Figure 5 was employed with: R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>13</sub> as CH<sub>2</sub>; and p ~ 3 to generate tri(ethylene glycol) methyl allyl ether (AMPEO<sub>3</sub>) as a side chain precursor. A solution of tri(ethylene glycol) methyl ether (98.4 g, 0.6 mol, Aldrich) was added dropwise to a suspension of NaH (60% dispersion in mineral oil, Acros Organics)(28.8 g, 0.72 mol) in THF (250 mL) chilled to 0 °C. This solution was stirred for an additional two hours followed by dropwise addition of allyl bromide (87.1 g, 0.72 mol, Aldrich). The resulting mixture was stirred overnight and then filtered so as to remove the NaBr product and excess NaH. Volatile materials were removed by rotary evaporation to yield an orange oil. Kugelrohr distillation at 80 °C and 0.5 torr was employed to collect 100 g of product.

[0071] EXAMPLE 2 (p~7.2)

[0072] The generalized reaction illustrated in Figure 5 was employed with: R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>18</sub> as CH<sub>2</sub>; and p ~ 7.2 to generate a poly(ethylene glycol) allyl methyl ether (APEO7.2) as a side chain precursor. A solution of poly(ethylene glycol) methyl ether (Aldrich, MPEO7.2, 105 g, 0.3 mol) in 250 mL of THF was added dropwise to a suspension of NaH (60% dispersion in mineral oil) (14.4 g, 0.36 mol) in THF (250 mL) chilled to 0 C. This solution was stirred for 2 hours followed by the dropwise addition of allyl bromide (43.5 g, 0.36 mol). The resulting mixture was stirred overnight and then filtered to remove the NaBr product and excess NaH. All volatile materials were removed by rotary evaporation to yield an orange oil. This oil was dissolved in water, and unreacted MPEO7.2 was extracted using 3x50 mL portions of toluene. The desired product was then extracted into chloroform from the water layer with 3x200 mL portions of CHCl<sub>3</sub>. This was dried with MgSO<sub>4</sub> and all volatile materials were removed by rotary evaporation. 99.4 g (85%) of product was collected by Kugelrohr distillation (180~280°C/0.5 torr).

[0073] EXAMPLE 3 (n ~ 6)

[0074] The generalized reaction illustrated in Figure 4 was employed with: R as methyl; R<sub>1</sub> as methyl; i as 4, j as 0, R<sub>16</sub> as hydrogen, m = 0 and n ~ 6 to generate a polysiloxane precursor. To a 100 mL flame-dried flask was added 13.43 g tetramethyldisiloxane (0.10 mole, 5 Gelest) and 48.10 g 1,3,5,7-tetramethylcyclotetrasiloxane ( $D_4^H$ ) (0.20 mole, Gelest). The flask was sealed by a rubber stopper. Fuming sulfuric acid (1.54 g, 2.5 wt%) was slowly dropped into the flask by a pipette as a cationic initiator. The mixture was heated to 50°C and kept at this temperature for 24 hours. The crude product was completely dissolved in diethyl ether and washed with 10% NaHCO<sub>3</sub> aqueous solution until neutral. The ether layer was dried for 48 h 10 over Na<sub>2</sub>SO<sub>4</sub> powder. After filtration, the ether was removed by rotovap, and then put under vacuum at 70°C overnight to remove any volatile materials. The n value was determined by the integration ratio of Si-H at 4.7 ppm to Si-CH<sub>3</sub> at 0.3 ppm from <sup>1</sup>H-NMR measurement (n ~ 6).

[0075] EXAMPLE 4 (n ~ 3)

[0076] The generalized reaction illustrated in Figure 4 was employed with: R as methyl; R<sub>1</sub> as methyl; i as 4, j as 01, R<sub>16</sub> as hydrogen, m = 0 and n ~ 3 to generate a polysiloxane precursor. To a 100 mL flame-dried flask was added 13.43 g (0.10 mole) tetramethyldisiloxane and 24.05 g (0.10 mole)  $D_4^H$ , then the flask was sealed with a rubber stopper. 0.94 g (2.5 wt. %) of fuming sulfuric acid was slowly dropped into the flask by a pipette, as a cationic initiator. 15 The mixture was heated to 50°C and kept at this temperature for 24 hours. The crude product was completely dissolved in diethyl ether and washed with 10% NaHCO<sub>3</sub> aqueous solution until neutral. The ether layer was dried for 48 h over Na<sub>2</sub>SO<sub>4</sub> powder. After filtration, the ether was removed by rotovap, and then put under vacuum at 50°C overnight to remove any volatile 20 materials (yield 85%). The n value was determined by the integration ratio of Si-H at 4.7 ppm to Si-CH<sub>3</sub> at 0.3 ppm from <sup>1</sup>H-NMR measurement (n~3). 25

[0077] EXAMPLE 5 (n ~ 3; p ~3)

[0078] The generalized reaction illustrated in Figure 1 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>11</sub> as CH<sub>2</sub>O with the O linked to the poly(ethylene

oxide) moiety;  $m = 0$ ;  $n \sim 3$ , and  $p \sim 3$  to generate a polysiloxane having side chains that include a spacer between the backbone and a poly(ethyleneoxide) moiety. To an oven-dried three-neck 500 mL flask was added 24.0 g of the polysiloxane precursor from Example 4 and 97.6 g (20% excess) of the AMPEO<sub>3</sub> from Example 1 by syringe. Dicyclopentadieneplatinum(II) dichloride 5 (500 ppm, ~2% in toluene) was added and the reaction solution was heated to 75°C for 24 hours and then cooled to room temperature. The excess AMPEO<sub>3</sub> and its isomers were removed by Kugelrohr distillation. The final product is a yellowish to brown colored liquid.

## [0079] EXAMPLE 6 (n ~ 6; p ~3)

10 [0080] The generalized reaction illustrated in Figure 1 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>11</sub> as CH<sub>2</sub>O with the O linked to the poly(ethylene oxide) moiety;  $m = 0$ ;  $n \sim 6$ , and  $p \sim 3$  to generate a polysiloxane having side chains that include a spacer between the backbone and a poly(ethyleneoxide) moiety. To an oven-dried three-neck 500 mL flask was added 12.0 g of the polysiloxane precursor from Example 3 and 48.8 g (20% excess) of the AMPEO<sub>3</sub> from Example 1 by syringe. Dicyclopentadieneplatinum(II) dichloride 15 (500 ppm, ~2% in toluene) was added and the reaction solution was heated to 75°C for 24 hours and then cooled to room temperature. The excess AMPEO<sub>3</sub> and its isomers were removed by Kugelrohr distillation. The final product is a yellowish to brown colored liquid.

## 20 [0081] EXAMPLE 7 (n ~ 6; p ~7.2)

[0082] The generalized reaction illustrated in Figure 1 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>11</sub> as CH<sub>2</sub>O with the O linked to the poly(ethylene oxide) moiety;  $m = 0$ ;  $n \sim 6$ , and  $p \sim 7.2$  to generate a polysiloxane having side chains that include a spacer between the backbone and a poly(ethylene oxide) moiety. To an oven-dried 25 three-neck 500 mL flask was added 12.0 g of the polysiloxane precursor of Example 3 and 48.8 g (20% excess) of the poly(ethylene glycol) allyl methyl ether (APEO7.2) side chain precursor of Example 2 by syringe. Dicyclopentadieneplatinum(II) dichloride (500 ppm, ~2% in toluene) was added and the reaction solution was heated to 75°C for 24 hours and then cooled to room

temperature. The excess side chain precursor and its isomers were removed by Kugelrohr distillation. The final product is a yellowish to brown colored liquid.

[0083] EXAMPLE 8 (n ~ 3; p ~7.2)

5 [0084] The generalized reaction illustrated in Figure 1 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>11</sub> as CH<sub>2</sub>O with the O linked to the poly(ethylene oxide) moiety; m = 0; n ~ 6, and p ~7.2 to generate a polysiloxane having side chains that include a spacer between the backbone and a poly(ethylene oxide) moiety. To an oven-dried three-neck 250 mL flask was added 12.0 g of polysiloxane precursor of Example 4 and 78.0 g of  
10 the poly(ethylene glycol) allyl methyl ether (APEO7.2) side chain precursor of Example 2 by syringe. Dicyclopentadieneplatinum(II) dichloride (500 ppm, ~2% in toluene) was added and the reaction solution was heated to 75 °C for 24 hours and cooled to room temperature. The excess side chain precursor and its isomers were removed by Kugelrohr distillation. The product is a yellowish to brown liquid, which was decolorized by activated charcoal in refluxing toluene.

15

[0085] EXAMPLE 9 (n ~ 6; p ~3)

20 [0086] The generalized dehydrogenation reaction illustrated in Figure 2 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>14</sub> as nil; m = 0; n ~ 6, and p ~3 to generate a polysiloxane having terminal side chains with a poly(ethylene oxide) moiety. A 250 mL Schlenk flask was flame-dried over nitrogen three times. To the flask was added 12.0 g of the polysiloxane precursor of Example 3 and 32.8 g tri(ethylene glycol) methyl ether (Aldrich, vacuum distilled prior to use) by a syringe. Dry toluene solvent (40 mL, distilled from Na and benzophenone) was injected to make a clear solution. Tri(pentafluorophenyl) borane (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, 0.0512 g, 0.05 mol% of Si-H) was dissolved in 10 mL toluene and the result injected into the  
25 precursor solution. The flask was heated to 70°C with vigorous magnetic stirring. The production of H<sub>2</sub> bubbles was observed during the stirring. Samples were taken and the progress of the dehydrogenation reaction was followed by FTIR measurements. After completion of the reaction, the excess alcohol was removed by Kugelrohr distillation. The

structure of the final product was confirmed by FTIR (no -OH absorption at 3400  $\text{cm}^{-1}$  or -Si-H at 2170  $\text{cm}^{-1}$ ). The product was sealed in a flask under argon for storage.

[0087] EXAMPLE 10 (n ~ 6; p ~5)

5 [0088] The generalized dehydrogenation reaction illustrated in Figure 2 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>14</sub> as nil; m = 0; n ~ 6, and p ~5 to generate a polysiloxane having terminal side chains with a poly(ethylene oxide) moiety. A 50 mL Schlenk flask was flame-dried over nitrogen three times. To the flask was added 1.5 g of the polysiloxane precursor of Example 3 and 6.3 g penta(ethylene glycol) methyl ether by a 10 syringe. Absolute toluene solvent (10 mL, distilled from Na and benzophenone) was injected to make a clear solution. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.0128 g, 0.05 mol% of Si-H) was dissolved in 5 mL toluene and the result injected into the precursor solution. The flask was heated to 70°C with vigorous 15 magnetic stirring and kept at this temperature overnight. The production of H<sub>2</sub> bubbles was observed during stirring. FTIR and <sup>1</sup>H-NMR measurements were taken to follow the progress of the dehydrogenation reaction. After completion of the reaction, the excess alcohol was removed by Kugelrohr distillation. The structure of the final product was confirmed by FTIR (no -OH absorption at 3400  $\text{cm}^{-1}$  or -Si-H at 2170  $\text{cm}^{-1}$ ) and was sealed in a flask under argon for storage.

20 [0089] EXAMPLE 11 (n ~ 6; p ~7.2)

[0090] The generalized dehydrogenation reaction illustrated in Figure 2 was employed with: R as methyl; R<sub>1</sub> as methyl; R<sub>7</sub> as hydrogen; R<sub>8</sub> as CH<sub>3</sub>; R<sub>14</sub> as nil; m = 0; n ~ 6, and p ~7.2 to generate a polysiloxane having terminal side chains with a poly(ethylene oxide) moiety. A 250 mL Shlenk flask was flame-dried over nitrogen three times. To the flask was added 12.0 g 25 of the polysiloxane precursor of Example 3 and 70.0 g poly(ethylene glycol) methyl ether (Aldrich, Mw = 350, dried by molecular sieves for 7 days) by a syringe. Absolute toluene solvent (10 mL, distilled from Na and benzophenone) was injected into the precursor solution to make a clear solution. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.0512 g, 0.05 mol% of Si-H) was dissolved in 10 mL toluene and the result injected into the precursor solution. The flask was heated to 70°C with vigorous

magnetic stirring. The production of H<sub>2</sub> bubbles was observed during stirring. FTIR measurements were taken to follow the progress of the dehydrogenation reaction. After completion of the reaction, excess alcohol was removed by addition of 5% excess of the polysiloxane precursor of Example 3. The structure of the final product was confirmed by 5 FTIR (no -OH absorption at 3400 cm<sup>-1</sup> or -Si-H at 2170 cm<sup>-1</sup>).

[0091] EXAMPLE 12

[0092] LiTFSI salt was dissolved in the polysiloxanes generated in Examples 5–10 to form a liquid electrolyte having an [EO]/[Li] = 15. The ionic conductivities of the electrolytes 10 were determined from AC impedance curves of 2032 button cells assembled by injecting the electrolyte between two stainless steel discs with a Teflon O-ring (1/32 inch thick) to prevent short circuits. The measurement frequency range was from 1 MHz to 10 Hz. The ionic conductivity results are presented in Table 1. For the purposes of comparison, Table 2 presents the 15 ionic conductivity results for polysiloxanes with similar structures and trimethylsilyl termination.

n	p	R <sub>9</sub>	[O]/[Li]	Ionic Conductivity (Rm. Temp. (~25 °C), S/cm)
3	p = 3	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	5.91 x 10 <sup>-5</sup>
6	p = 3	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	6.74 x 10 <sup>-5</sup>
6	p = 7.2	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	1.31 x 10 <sup>-4</sup>
3	p = 7.2	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	1.59 x 10 <sup>-4</sup>
3	p = 3	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	2.00 x 10 <sup>-4</sup>
6	p = 3	O	15	1.20 x 10 <sup>-4</sup>
6	p = 5	O	15	1.07 x 10 <sup>-4</sup>

**Table 1**

n	p	R <sub>9</sub>	[O]/[Li]	Ionic Conductivity (Rm. Temp., S/cm)
6	p = 3	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	9.46 x 10 <sup>-5</sup>
6	p = 7.2	-(CH <sub>2</sub> ) <sub>3</sub> -O-	15	7.12 x 10 <sup>-5</sup>
6	p = 3	O	15	1.07 x 10 <sup>-4</sup>

**Table 2**

[0093] The electrolytes described above can be used in electrochemical devices. For instance, the electrolytes can be used as the electrolyte of batteries, capacitors, and hybrid capacitor/batteries. As an example, the electrolyte can be applied to batteries in the same way 5 as carbonate-based electrolytes. Batteries with a liquid electrolyte can be fabricated by injecting the electrolyte into a spiral wound cell or prismatic type cell. The electrolyte can be also coated onto the surface of electrodes and assembled with a porous separator to fabricate a single or multi-stacked cell that can enable the use of flexible packaging.

[0094] The solid and/or gel electrolytes described above can also be applied to 10 electrochemical devices in the same way as solid carbonate-based electrolytes. For instance, a precursor solution having components for a solid electrolyte can be applied to one or more substrates. Suitable substrates include, but are not limited to, anodes, cathodes and/or separators such as a polyolefin separator, nonwoven separator or polycarbonate separator. The precursor solution is converted to a solid or gel electrolyte such that a film of the electrolyte is 15 present on the one or more substrates. In some instances, the substrate is heated to solidify the electrolyte on the substrate. An electrochemical cell can be formed by positioning a separator between an anode and a cathode such that the electrolyte contacts the anode and the cathode.

[0095] An example of a suitable lithium battery construction includes one or more lithium metal oxide cathodes, one or more porous separators, and one or more anodes made of 20 carbon, lithium metal, or combinations thereof. Cathodes may include Li<sub>x</sub>VO<sub>y</sub>, LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiNi<sub>1-x</sub>Co<sub>y</sub>Me<sub>z</sub>O<sub>2</sub>, LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub>, LiMn<sub>0.3</sub>Co<sub>0.3</sub>Ni<sub>0.3</sub>O<sub>2</sub>, LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFeO<sub>2</sub>, LiMc<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, vanadium oxide, carbon fluoride and mixtures thereof. Me is Al, Mg, Ti, B, Ga, Si, Mn, or Zn, and combinations thereof. Mc is a divalent metal such as Ni, Co, Fe, Cr, Cu and combinations thereof. Anodes may include graphite, soft carbon, hard carbon, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,

tin alloys, silica alloys, intermetallic compounds, lithium metal, lithium metal alloys, and combinations thereof.

[0096] Although Figure 1 through Figure 3 are illustrated with components that include poly(ethylene oxide) moieties, these reactions can be performed using other poly(alkylene oxide) 5 moieties.

[0097] Other embodiments, combinations, and modifications of this invention will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, this invention is to be limited only by the following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying 10 drawings.